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AUTHOR(S):

Tanimoto, Takashi; Nakano, Takato

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**Stress relaxation of wood partially non-crystallized
using aqueous NaOH solutions**

Takashi Tanimoto¹

Takato Nakano^{2*}

¹: Laboratory of Biomaterials Design, Division of Forest and Biomaterials Science, Graduate School of
Agriculture, Kyoto University, Kita-Shirakawa, Kyoto, 606-8502 Japan

*: corresponding author

Laboratory of Biomaterials Design, Division of Forest and Biomaterials Science, Graduate School of
Agriculture, Kyoto University, Kita-Shirakawa, Kyoto, 606-8502 Japan

Tel.: +81-75-753-6234

.e-mail address: tnakano@kais.kyoto-u.ac.jp.

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Stress relaxation

Relaxation rate

X-ray diffraction

crystallinity

NaOH solution

High lights

>We examine the effect of the crystallinity on the mechanical properties of wood. >The relaxation
modulus and relaxation rate decreased with decreasing crystallinity. >The crystallinity dependence
on the relaxation rate increased with increasing time. >Non-crystallized regions formed along the
microfibril longitudinal axis.

Abstract

Wood samples (*Picea jezoensis* Carr.) were treated with aqueous NaOH solutions (0–0.20 concentration fraction, 12 conditions), and bending tests were performed to measure stress relaxation. The relationship between mechanical properties and NaOH concentration is discussed. The relaxation modulus and relaxation rate were divided into three concentration ranges. Both decreased slightly for NaOH concentrations less than 0.10, decreased drastically for concentrations between 0.11 and 0.14, and decreased slightly for concentrations greater than 0.15. The change in relaxation behavior upon NaOH treatment was due to an increase in molecular chain mobility in non-crystallized regions along the microfibril longitudinal axis in wood as well as lignin swelling. Furthermore, the molecular chain response in this region required time; thus, the dependence of crystallinity on the relaxation rate was apparent in the long time region.

Introduction

Wood treated with aqueous NaOH shows an anisotropic dimensional change, especially along the longitudinal axis, and the contraction depends on the alkali concentration. The researcher who discussed this phenomenon in detail for the first time was Stöckmann (1971a, 1971b), who pointed out the need for microfibril contraction based on thermodynamic considerations. Contraction is induced by NaOH and other alkaline solutions (Nakano, 1988a, 1988b, 1989), and the degree of contraction depends on the type and concentration of the alkaline solution and increases as $\text{NaOH} < \text{KOH} < \text{LiOH}$ at the same concentration. Nakano et al. (2000) reported an experimental temperature dependence of longitudinal contraction and showed that contraction depends on a change in the ultrastructure of the cell wall, especially the non-crystallization of microfibrils. That is, contraction is due to a non-crystallized region along the microfibril longitudinal axis and the entropy elastic force caused by the non-crystallization of cellulose microfibril helical winding in cell walls. Moreover, Nakano (2010) formulated a relationship between anisotropic dimensional changes and the crystallinity change due to alkali treatment.

The treatment of native cellulose with NaOH aqueous solution has been well-known as mercerization and industrially used so long time. Cellulose exhibits various polymorphism with NaOH treatment (Okano et al., 1984; Fink et al., 1985) and changes its crystallinity during their processes (Fengel et al., 1995; Zhou et al., 2003; Ouajai et al., 2004). Cellulose in wood also examined the effect of NaOH treatment with NaOH solution on the structure. Revol et al. (1981) and Shiraishi et al. (1984) reported that the cellulose structure in wood hardly changed due to matrix consisted of lignin and hemicellulose. Most of these studies were examined at higher concentration of NaOH.

The mechanical behavior of alkali-treated wood also depends on the concentration of the alkaline solution. Stress-strain behavior depends on the alkali concentration and shows marked changes for NaOH concentrations between 0.10 and 0.13 (Nakano, 1989, 2000). Relaxation behavior during alkali treatment has also been reported (Nakano, 1988); however, the samples were oven-dried, and the effects of collapse were not considered. Also, the change in relative crystallinity was not discussed.

In the present study, mechanical relaxation behavior and crystallinity index were measured, and the effect of wood non-crystallization by NaOH treatment on mechanical relaxation behavior is discussed.

Experimental

Materials and NaOH treatment

Wood samples were prepared from Yezo spruce (*Picea jezoensis* Carr.) with rectangular dimensions of 70 (L) × 7.5 (R) × 2 (T) (mm), where L, R, and T are the longitudinal, radial, and tangential directions, respectively. Samples were oven-dried at 60°C under vacuum for 1 day. The weight and dimensions of the oven-dried samples were measured; they were then soaked in aqueous NaOH solutions (0–0.20 concentration fraction) and stored at room temperature for 2 days, after which they were washed in distilled water for 2 weeks. The weight and dimensions of the treated samples were measured again. Three samples were treated using each NaOH concentration, and two unwarped samples were selected: one was subjected to stress relaxation measurements and the other was analyzed using X-ray diffraction (XRD). The sample selected for stress relaxation measurements remained in distilled water until the measurements were taken.

Stress relaxation measurements

Stress relaxation measurements were conducted in water at 25°C using a three-point center concentrated-load bending test with a span of 50 mm. The displacement of 0.27 mm was less than one-third of the proportional displacement limit for the samples, which was applied to the LR-plane. The measurement period was about 24 hours, and the relaxation modulus was calculated as a function of time based on the measurement load.

X-ray analysis

Alkali-treated samples were freeze-dried under vacuum overnight after being frozen with liquid nitrogen. Freeze-dried samples were oven-dried at 60°C under vacuum over P₂O₅ for 1 day. The diffraction patterns were obtained for the LR-plane at room temperature by a Rigaku Ultima IV, set to 40 kV and 40 mA in the scanning range of 5–35°. The relative crystallinity of the samples was calculated from the diffraction profile in the range of 10–28°. That is, X-ray diffraction profile was isolated to a crystalline part and a non-crystalline part using commercial software the PeakFit (SeaSolve Software, Inc.) for peak isolation and then each area and the whole area were calculated. The relative crystallinity was calculated as the proportion of the area of crystalline part to the whole area of the scattering area (Iwamoto et al. 2007).

Results and Discussion

Studies on the characteristic changes in mechanical behavior and dimension after alkali treatment have reported that structural changes in wood microfibrils are a key factor (Nakano, 1988, 1989, 2000, 2010). Moreover, the relative crystallinity of wood microfibrils reportedly decreases due to alkali

treatment. Additionally, wood microfibrils do not undergo a lattice transformation from cellulose I to cellulose II; the cellulose alone changes. Thus, we start by discussing the lattice transformation of the samples.

Lattice transformation during alkali treatment is discussed based on XRD analysis. Figure 1 shows typical X-ray diffractograms, and Figure 2 illustrates the relationship between the NaOH concentration and the relative crystallinity. A lattice transformation from cellulose I to cellulose II during alkali treatment is well-known to not occur in wood (Revol et al. (1981), Shiraishi et al. (1984)), and Figure 1 confirms that the lattice transformation did not take place. However, the relative crystallinity was nearly constant for concentrations less than 0.10 but decreased with increasing concentration above 0.11. This dependence on alkali concentration is consistent with previous reports (Ishikura, 2010; Nakano, 2010).

The proportion of microfibrils and the fibril angle influence the mechanical properties of wood. Fujimoto et al. (2000) reported that the fibril angle increased slightly for NaOH concentrations between 0.10 and 0.15 in alkali-treated Yezo spruce samples, and Nakano (2010) stated that the fibril angle changed little during alkali treatment. In the present study, the change in the fibril angle appears to be slight. Based on the study of Reiterer et al. (1999) on the relationship between Young's modulus and fibril angle, our result was probably due to a decrease in crystalline cellulose, which has a high Young's modulus. Thus, the change in fibril angle is neglected in the following discussion.

Figure 3 shows relaxation curves for each NaOH concentration. Plots of $E(t)$ vs. $\ln(t)$ did not show a clear difference in relaxation behavior, but the relaxation modulus displayed characteristic concentration dependence.

Previous studies have demonstrated that the concentration dependence of the relaxation modulus was due to an internal structural change during alkali treatment. Figure 4 shows the dependences of the relaxation modulus at $\ln(t) = 0$ and the dimensional change along the longitudinal axis on NaOH concentration and the degree of crystallinity. Both show similar concentration and crystallinity dependence, indicating that both changes were due to the same factor, i.e., the change in relative crystallinity.

The concentration dependence of the relaxation modulus in Figure 4 was divided into three ranges. The relaxation modulus decreased slightly for NaOH concentrations less than 0.10, decreased considerably for concentrations between 0.11 and 0.14, and decreased slightly for concentrations greater than 0.15. This result is consistent with a previous report (Nakano et al., 2000). Nakano et al. (2000) showed that the longitudinal contraction in wood during alkali treatment was due to a non-crystallized region along the microfibril longitudinal axis, and that contraction was due to the entropy elastic force because of an increase in the heating temperature. Additionally, Nakano (2010) reported that anisotropic swelling during alkali treatment can be explained by the

154 aforementioned mechanism. Similar relationships between the relaxation modulus and the
155 dimensional change along the longitudinal axis on the NaOH concentration and the degree of
156 crystallinity are consistent with the above discussion.

157 Considering the change in relative crystallinity, a decrease in the relaxation modulus for
158 NaOH concentrations less than 0.10 (Fig. 4) was not due to the change in relative crystallinity. It
159 probably occurred because of an increase in the geometrical moment of inertia during alkali treatment,
160 which increased linearly for NaOH concentrations less than 0.10 and was nearly constant for
161 concentrations greater than 0.11.

162 The concentration dependence of the relaxation modulus in Figure 3 suggests that
163 non-crystallization due to alkali treatment affected the relaxation modulus during measurements.
164 This makes comparison among the relaxation spectra difficult because the relaxation modulus
165 changed drastically during alkali treatment, and comparing the change in relaxation behavior using
166 an absolute value is difficult. Thus, relaxation behavior was evaluated based on the relaxation rate,
167 $d \ln E(t) / d \ln t$. This value represents the relaxation level at each time, making the change in
168 relaxation behavior clear.

169 Figure 5 shows $d \ln E(t) / d \ln t$ vs. $\ln(t)$. The relaxation rate was divided into three
170 concentration ranges: non-alkali treated (0), 0.03–0.12, and greater than 0.13. The concentration
171 ranges correspond to the three ranges in Figure 4. That is, the relaxation behavior changed due to
172 non-crystallization during alkali treatment. Figure 5 shows that the absolute relaxation rate
173 increased in the long time region for NaOH concentrations less than 0.12, and that the rate increased
174 in the short and long time regions for concentrations greater than 0.13.

175 The relationship between the relaxation rate and relative crystallinity is shown in Figure 6.
176 The relaxation rate changed markedly for relative crystallinities between 0.30 and 0.33. Although
177 the relaxation modulus changed considerably, the relaxation rate changed slightly in the short time
178 region but significantly in the long time region. The relaxation rate at $\ln(t) = 11$ changed
179 considerably for relative crystallinities between 0.30 and 0.33. Additionally, the long-term relaxation
180 rate recovered for relative crystallinities of less than 0.30. For relative crystallinities greater than
181 0.33 or for NaOH concentrations less than 0.12, the relaxation rate changed little, regardless of time.

182 The mechanism of the change in relaxation behavior with decreasing relative crystallinity is
183 discussed. Two mechanisms must be considered: one is a crystallinity dependence on the relaxation
184 modulus (Fig. 4), and the other is a crystallinity dependence on the relaxation rate (Fig. 6). The
185 former is not time-dependent, but the latter is.

186 The former increases the region reacting to deformation promptly, namely the
187 non-crystallized region. That is, the decrease in the relaxation modulus at $\ln(t) = 0$ with increasing
188 NaOH concentration was due to a decrease in the fraction of the crystallized region (Fig. 4), which was

rigid, and an increase in the fraction of the non-crystallized region, which was flexible. Another factor is a decrease in the contribution of lignin, which binds microfibrils. The interaction between microfibrils and lignin is believed to have been weakened by swelling during alkali treatment. Alkali solution causes dissolution of hemicellulose, but dissolution was nearly complete at a NaOH concentration of 0.05 and did not increase for concentrations greater than 0.05. Thus, dissolution scarcely affected the mechanical properties.

The relaxation rate depended on the response of molecular chain rearrangement. Figure 6 shows that the crystallinity dependence on the relaxation rate increased with increasing $\ln(t)$, suggesting that molecular chain rearrangement required time, and that the change in the relaxation rate related to the restricted molecular chain motion. Furthermore, the relaxation rate did not change for relative crystallinities greater than 0.33 but did change for relative crystallinities less than 0.33, suggesting that the molecular chain response required a large non-crystallization region. Thus, non-crystallized regions formed along the microfibril longitudinal axis. The motion of non-crystallized regions around the microfibrils appears to be restricted by crystalline regions parallel to the longitudinal axis.

Nakano et al. (2000) proposed that a reduction in the end-to-end distance of the chain segments in the amorphous regions was due to longitudinal contraction of microfibrils caused by alkali solution penetrating the defects in the microfibrils longitudinal direction. For the experimental method used in this study (three-point bending tests), contractive and tensional stress occurred. The S2-layer, which is about 0.80 fraction occupation of the cell wall, so that it dominates the mechanical properties of wood. The result shown in Figure 4 suggests that the alkali solution penetrated the defects in the microfibril longitudinal direction, and that a non-crystallized region was formed along the longitudinal axis for softwood, in which the fibril angle of the S2-layer is small. Furthermore, molecular chain rearrangement in this region requires time; thus, the crystallinity dependence on the longer time relaxation rate (Fig. 6) was evident.

Conclusion

The effect of the crystallinity change induced by NaOH treatment on the mechanical relaxation behavior of wood was investigated. The relaxation modulus and relaxation rate were divided into three concentration ranges. Both decreased slightly for NaOH concentrations less than 0.10, decreased markedly for concentrations between 0.11 and 0.14, and decreased slightly for concentrations greater than 0.15. This was due to an increase in the molecular chain mobility in non-crystallized regions along the microfibril longitudinal axis in wood and lignin swelling due to the

224 NaOH treatment. Furthermore, molecular chain rearrangement in this region requires time; thus,
225 the crystallinity dependence on the longer time relaxation rate was apparent.
226

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Figure captions

Figure 1. Typical X-ray diffractograms of untreated and treated wood using aqueous NaOH solutions.

Figure 2. Relationship between crystallinity and NaOH concentration.

Figure 3. Stress relaxation curves of samples treated with various NaOH solutions. Note: numbers indicate NaOH concentration fractions.

Figure 4. Dependence of the relaxation modulus at $\ln(t/s) = 0$ and the dimensional change along the longitudinal direction on NaOH concentration and relative crystallinity.

Figure 5. Relaxation rate, $d \ln E(t) / d \ln[t]$, of samples treated with various NaOH concentrations.

Figure 6. Dependence of the relaxation rate at $\ln(t/s) = 3, 8,$ and 11 on relative crystallinity.

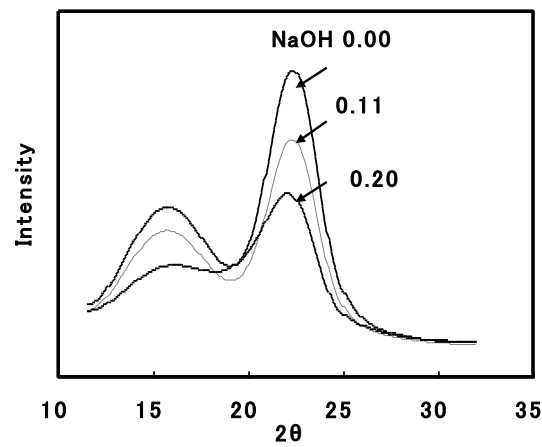


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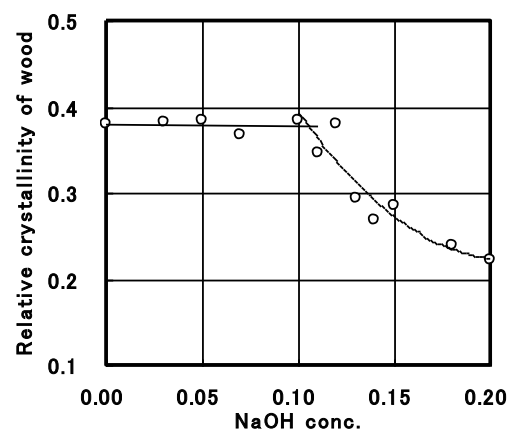


Figure 2. Relationship between crystallinity and NaOH concentration.

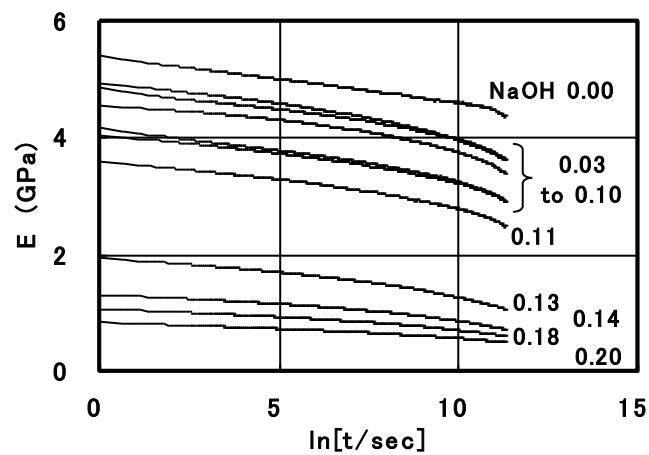


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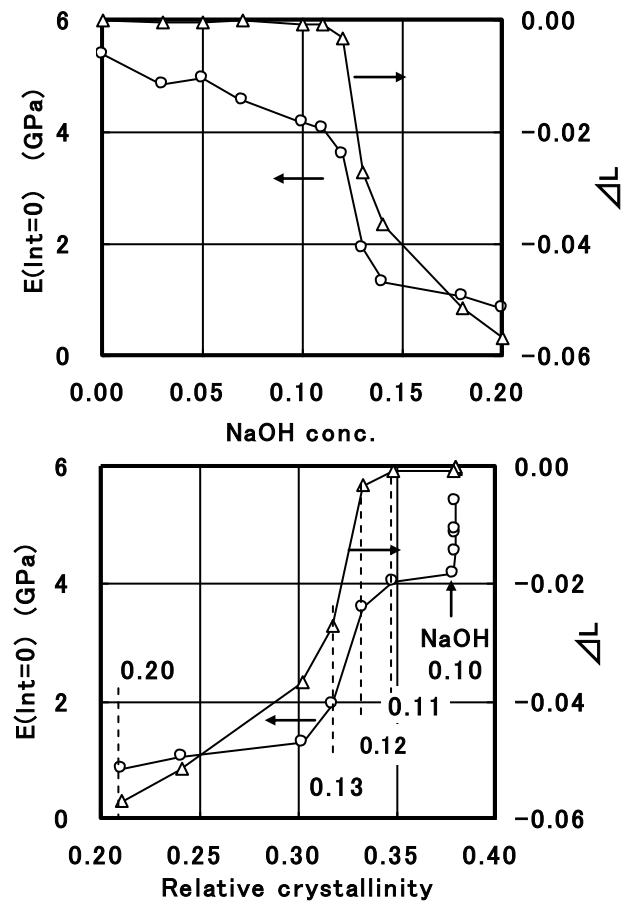


Figure 4. Dependence of the relaxation modulus at $\ln(t/s) = 0$ and the dimensional change along the longitudinal direction on NaOH concentration and relative crystallinity.

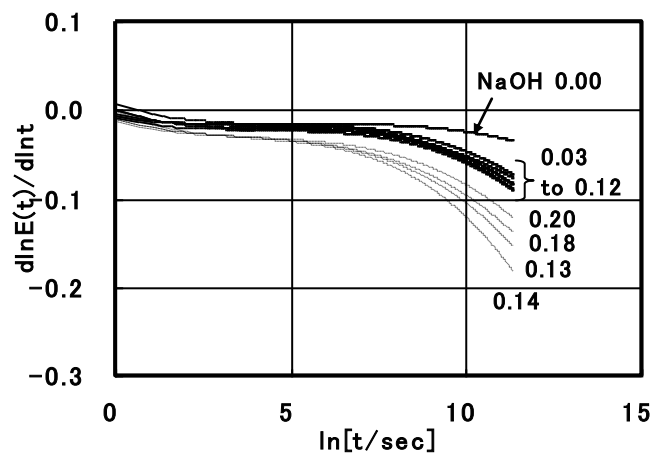


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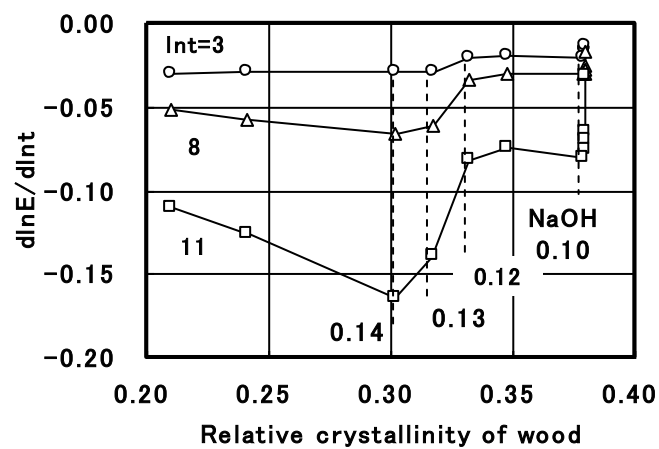


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